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Review

Biochar stability assessment methods: A review

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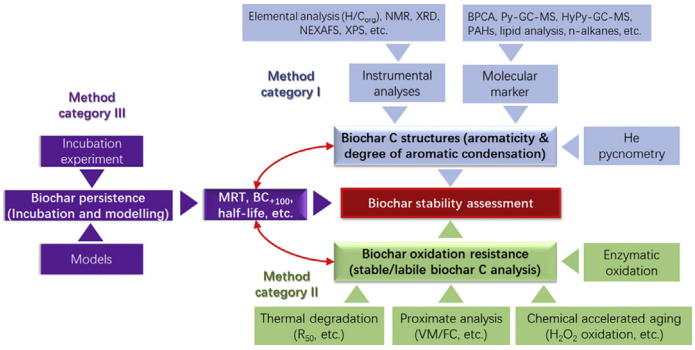
HIGHLIGHTS

- Stability assessment methods are important to biochar carbon sequestration.
- Biochar stability assessment methods were classified into three categories.
- Method details, advantages and disadvantages, correlations were reviewed.
- Elemental and proximate analyses, thermal oxidation, NMR C structure are promising.

GRAPHICAL ABSTRACT


Elemental analysis (H/Corg), NMR, XRD, NEXAFS, XPS, etc.
BPCA, Py-GC-MS, HyPy-GC-MS, PAHs, lipid analysis, n-alkanes, etc.
Method category I
Instrumental analyses
Molecular marker
Method category III
Incubation experiment
Biochar C structures (aromaticity & degree of aromatic condensation)
He pycnometry
Biochar persistence (Incubation and modelling)
MRT, BC+100, half-life, etc.
Biochar stability assessment
Models
Biochar oxidation resistance (stable/labile biochar C analysis)
Enzymatic oxidation
Method category II
Thermal degradation (R50, etc.)
Proximate analysis (VM/FC, etc.)
Chemical accelerated aging (H2O2 oxidation, etc.)

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ABSTRACT

Biochar is being developed as a candidate with great potential for climate change mitigation. Sequestering biochar carbon in soil contributes greatly to the reduction of greenhouse gases emissions, and biochar stability is the most decisive factor that determines its carbon sequestration potential. However, methods that can be used universally for direct or indirect assessment of biochar stability are still under investigation. This present review aims to give comprehensive and detailed up-to-date information on the development of biochar stability assessment methods. The method details, advantages and disadvantages, along with the correlations between different methods were reviewed and discussed.

Three stability assessment method categories were identified: I) biochar C structure analysis, II) biochar oxidation resistance determination, and III) biochar persistence evaluation by biochar incubation and mineralization rate modelling. Biochar persistence value (e.g., mean residence time, MRT) obtained from incubation and modelling and biochar elemental ratios such as H/C_{org} and O/C_{org} are the current most commonly used biochar stability indicators. Incubation and modelling method is too time-consuming while H/C_{org} and O/C_{org} ratios are qualitative and conservative, although the effectiveness of these two methods can be further improved. On the other hand, biochar C structures such as aromaticity and degree of aromatic condensation obtained from nuclear magnetic resonance (NMR) analysis and benzene polycarboxylic acids (BPCA) molecular markers and biochar oxidation/degradation recalcitrance obtained from proximate analysis (volatile matter and fixed carbon yields), thermal recalcitrance index (R_{50}), and H_2O_2- and heat-assisted oxidation (Edinburgh stability tool) are being developed as promising proxies to indicate biochar stability.

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Contents

1. Introduction . . . 211
2. Biochar properties and biochar stability . . . 212
3. Biochar stability assessment by C structure analysis . . . 212
   - 3.1. Ultimate analysis . . . 212
     - 3.1.1. H/C ratio . . . 212
     - 3.1.2. O/C ratio . . . 212
     - 3.1.3. Van Krevelen diagram . . . 213
   - 3.2. C structure analysis by instrumental methods . . . 213
     - 3.2.1. Nuclear magnetic resonance (NMR) analysis . . . 213
     - 3.2.2. X-ray diffraction (XRD) analysis . . . 214
     - 3.2.3. Near-edge X-ray absorption fine structure (NEXAFS) . . . 214
     - 3.2.4. X-ray photon spectroscopy (XPS) . . . 214
     - 3.2.5. Fourier transform infrared spectroscopy (FTIR) . . . 214
     - 3.2.6. Infrared diffuse reflectance spectroscopy in the near- or mid-infrared spectral range (NIRS/MIRS) . . . 214
   - 3.3. C structure analysis by molecular markers . . . 214
     - 3.3.1. Polycyclic aromatic hydrocarbons (PAHs) . . . 215
     - 3.3.2. Benzene polycarboxylic acids (BPCA) . . . 215
     - 3.3.3. Lipid analysis . . . 215
     - 3.3.4. *n*-Alkanes . . . 215
     - 3.3.5. Pyrolysis-GC–MS (Py-GC–MS) . . . 215
     - 3.3.6. HydroPyrolysis-GC–MS (HyPy-GC–MS) . . . 216
   - 3.4. C structure analysis by He pycnometry . . . 216
4. Biochar stability assessment by analyzing labile/stable biochar C . . . 216
   - 4.1. Proximate analysis . . . 216
     - 4.1.1. Fixed carbon (FC) or volatile matter (VM) . . . 216
     - 4.1.2. FC and VM . . . 216
   - 4.2. Thermal degradation . . . 216
     - 4.2.1. Temperature-programmed oxidation (TPO) . . . 217
     - 4.2.2. Recalcitrance index (R_{50}) . . . 217
   - 4.3. Chemically accelerated aging . . . 217
     - 4.3.1. H_2O_2- and heat-assisted oxidation (Edinburgh stability tool) . . . 217
     - 4.3.2. Dichromate ($K_2Cr_2O_7$) oxidation . . . 218
     - 4.3.3. Permanganate ($KMnO_4$) oxidation . . . 218
     - 4.3.4. Other chemical aging methods . . . 218
5. Biochar stability assessment by biochar incubation and modelling . . . 218
6. Perspectives and conclusions . . . 220

Acknowledgements . . . 220
Appendix A. Supplementary data . . . 220
References . . . 220

1. Introduction

Biomass is a term for organic material that stems from organisms which stores energy (mainly carbon) in it (McKendry, 2002), for which reason biomass has been widely studied and applied as feedstock to produce solid, liquid, or gas fuels for replacement of fossil fuels (Leng et al., 2018a, 2018b; H. Li et al., 2018; Y. Li et al., 2018; T. Wang et al., 2018; Y. Wang et al., 2018). On the other hand, the carbon in biomass that decomposes easily in nature can also be stored "permanently" (>100 years) as biochar (or bio-char) for after thermochemical treatment such as pyrolysis, gasification, and carbonization (Laird et al., 2009; Leng et al., 2015b). Pyrolysis, a thermochemical treatment processed at temperature 300–1000 °C in the absence of oxygen without solvent involvement (Anca-Couce, 2016; Tan et al., 2015; Wang et al., 2017; Zhang et al., 2016), is the most commonly used and effective process to produce preferable biochar (pyrogenic organic matter) from biomass to achieve the goal of climate change mitigation (Laird et al., 2009).

In fact, biochar application in soil is becoming a tool of great potential for the mitigation of climate change and protection of soil environment by carbon sequestration, greenhouse gases emission mitigation, soil remediation and conservation, and crop yield enhancement (Lehmann, 2007a, 2007b; Lehmann et al., 2006). The use of biochar as a carbon sequester assumes that stable carbon in biochar produced from biomass can persist in soil for hundreds or even thousands of years. Biochar stability or biochar's resistance to biotic and abiotic degradations in soil can be used for the description of the carbon sequestration potential of a biochar. Increasing studies have been carried out to investigate biochar stability trying to define and/or evaluate the biochar stability (Fig. S1). Previously, pyrolysis temperature was used as an indicator for biochar stability. However, it is too simple and inaccurate. Then O/C molar ratios proposed by Spokas (2010) as an indicator for biochar stability in soils serve a more robust proxy than biochar production parameters (e.g., pyrolysis temperature and biomass type). The International Biochar Initiative (IBI), a member-based organization with over 400 paid members around the world led by several outstanding scientists such as Johannes Lehmann (co-founder of IBI) who linked charcoal to soil application and firstly used the word "biochar" (Lehmann et al., 2006), later led the effort and gathered fourteen world-class experts in different fields of biochar stability and reviewed briefly stability assessment methods available by that time (Budai et al., 2013) and proposed the H/C_{org} mole ratio as the indicator for biochar stability (IBI, 2015). Whereas, European Biochar Foundation (EBC) made requirement on both of the H/C_{org} and O/C_{org} ratios to ensure biochar stability information (EBC, 2012). On the other hand, many other biochar stability assessment methods are still under exploration.

Over all, the stability evaluation methods can be divided into three categories: I) the qualification or quantification, directly or indirectly, of biochar C structures such as aromaticity or degree of aromatic

condensation by instrumental analyses such as elemental analysis and nuclear magnetic resonance (NMR) analysis or by molecular markers such as benzene polycarboxylic acids (BPCA); II) the qualification or quantification of the labile C or stable C (recalcitrant C) by thermal/chemical or thermochemical oxidation resistance methods such as proximate analysis, thermal degradation, and chemical oxidation; III) biochar persistence assessed by biochar incubation in soil and C mineralization modelling. Incubation and modelling is a biochemical method to make biochar stability assessment and it is generally regarded as the basis of the other two methods. Results from method categories I and II (biochar characterization) are indirect stability values and are indicative of biochar stability because of their close correlations with data obtained from incubation and modelling (biochar persistence in soil).

This present review aims to give comprehensive detailed up-to-date information on the development methods studied for biochar stability assessment. The method details, advantages and disadvantages, along with the correlations between different methods were also reviewed and discussed.

2. Biochar properties and biochar stability

A defining property of chars including biochar is the aromatic C structure which includes an amorphous phase (randomly organized aromatic rings) and a crystalline phase (condensed polyaromatic sheets) (Wiedemeier et al., 2015a). Therefore, the assessment of biochar stability can be the evaluation of the stability of the C in biochar or the proportion of stable C structures. Thus, C structure is the most decisive factor that determines biochar stability. Aromaticity and degree of aromatic condensation are useful indicators for the C structures of biochar (Wiedemeier et al., 2015a). Biochar of high aromaticity and/or degree of aromatic condensation are more likely to resist biological and thermochemical degradation and thus has high stability (Lehmann and Joseph, 2015). Aromaticity and/or degree of aromatic condensation of biochar can be indicative of the biotic and abiotic degradability of biochar in soil (B.P. Singh et al., 2012). They can be evaluated by carbon-carbon bonds analysis by instruments such as solid-state ^{13}C Nuclear magnetic resonance spectroscopy (NMR) (McBeath et al., 2011; Wiedemeier et al., 2015a) or by analysis of molecular makers, e.g., benzene polycarboxylic acids (BPCA) (McBeath et al., 2011). In fact, the elemental compositions of biochar are indicative of the carbon-carbon bonds or aromatic C content (aromaticity). For example, the molar H/C ratio is indicative of the degree of unsaturation or the amount of C═C double bonds by calculating the H deficiency relative to a saturated species (C_nH_{n+2}), and the number of aromatic rings may be further calculated.

Reactivity of the C structure such as the functionality (functional groups on C chains) and other degradation-related components of biochar are also important to biochar stability. The reactive functional groups along with the non-aromatic C structures constitute the main part of the labile biochar fraction and are vulnerable to biochemical (biotic) and/or physicochemical (abiotic) degradations in soil (Cross and Sohi, 2013; Harvey et al., 2012; Zimmerman, 2010). High functionality, e.g., high content of O- and/or N-containing functional groups can increase the reactivity of biochar, resulting in reduced biochar stability. Functionality can be analyzed by instruments such as Fourier transform infrared spectroscopy (FTIR) (Keiluweit et al., 2010; Knicker et al., 2007). On the other hand, the biochar oxidation resistance or the labile biochar fraction which includes labile non-aromatic C structures and reactive functional groups, etc. can be determined by thermal/chemical or thermochemical treatment such as proximate analysis and H_2O_2- and heat-assisted oxidation (Edinburgh stability tool) (Cross and Sohi, 2013).

Additionally, particle size (Bruun et al., 2012), minerals (Yang et al., 2016), sorption phenomena, pH, and physical properties such as pore structure and surface area of biochar may also influence the biochar stability. These biochar properties, along with the aforementioned aromaticity, degree of aromatic condensation, and labile/stable C, are mainly controlled by the properties (e.g., particle size) and compositions of the feedstock that is used for biochar production and the production process parameters such as heat treatment temperature (HTT), heating rate, residence time, pressure, catalyst, and reactors (Chen et al., 2016a, 2016b; Cross and Sohi, 2013; Keiluweit et al., 2010; Manyà et al., 2014a; Woolf et al., 2017). Processing of lignocellulosic biomass with high content of lignin at high HTT tends to produce biochar of high stability. In addition to the influence of biochar properties on biochar stability, soil environment such as soil organic carbon, minerals, microorganisms, pH, temperature, and moisture and the crops and plants growing on it can also affect significantly the mineralization of biochar in soil (Cheng et al., 2008; Fang et al., 2015; Lehmann and Kleber, 2015; Windeatt et al., 2014; Zimmerman, 2010; Zimmermann et al., 2012). Incubation of biochar in soil is to study the comprehensive biochar mineralization performance under the complicated soil-biochar matrix. In fact, analyses of aromaticity, degree of aromatic condensation, and labile/stable C of biochar are only results of physicochemical stability of biochar without analyzing the effects of soil and environment on its stability. These physicochemical stability values, however, can be correlated with the actual biochar persistence in soil by relating the properties to the results obtained from incubation and modelling studies. For example, ratio of H/C_{org} (Budai et al., 2013), H_2O_2- and heat-assisted oxidizable biochar fraction (Cross and Sohi, 2013), thermal recalcitrance (Harvey et al., 2012), and nonaromatic C proportion and degree of aromatic condensation (B.P. Singh et al., 2012) have been successfully correlated to the results from incubation and modelling, e.g., mean residence time (MRT) and mineralized biochar C proportion.

3. Biochar stability assessment by C structure analysis

3.1. Ultimate analysis

3.1.1. H/C ratio

H/C ratio is an ideal indicator for biochar C structure. Carbon stability in biochar indicated by the molar ratio of H/C_{org} has been adopted by IBI. The upper H/C_{org} limit of 0.7 is imposed to assure abundant fused aromatic ring structures and to distinguish biochar from the raw feedstocks or from other materials which are only partially or deficiently carbonized (IBI, 2015). It is a conservative value, based on several incubation experiments and their modelling results, to ensure that 50% (95% confidence) of biochar C could remain stable in soil after 100 years (Budai et al., 2013). Some detailed information can be found in ref. (Budai et al., 2013), in which H/C_{org} is justified as the most applicable proxy for biochar stability since then.

Total C is a general property for biochar. The modification made to use the organic C values rather than total C for biochar stability is due to the presence of inorganic carbonates in some high-ash biochars, and these inorganic carbonates do not form aromatic groups (IBI, 2015). However, only limited data are available for C_{org} in the literatures, with total C being reported in general because of easier availability. This will lead to considerable variation of stability results since sometimes C_{org} and total C will be distinctive when inorganic carbon appears in the biochar. The differences were found notable when a high degree of ash presented in biochars from poultry manure and paper mill waste, although the differences were much smaller for a wide range of biochars from woody and grass feedstocks (Enders et al., 2012). Additionally, there are also studies trying to modify H with H_{org} to exclude inorganic H bound to elements other than C (e.g., silicate) (Wang et al., 2013).

3.1.2. O/C ratio

Both O/C_{org} and H/C_{org} ratio values are required by EBC, a voluntary industry standard in Europe, to indicate biochar stability. The upper O/C_{org} limit of 0.4 and H/C_{org} limit of <0.7 requirements are used for a

standard-compliant biochar (EBC, 2012). Spokas (2010) claimed, biochar of different O/C ratio has different stability: biochars with an O/C molar ratio of <0.2 are typically the most stable, possessing an estimated half-life of >1000 years; biochars with an O/C ratio of 0.2–0.6 have intermediate half-lives of 100–1000 years; and, finally biochars with an O/C ratio of >0.6 possess a half-life in the order of <100 years.

H/C_{org} ratio is preferred over the O/C_{org} in IBI is because H is determined experimentally, while O is a value calculated by difference (O = 100 − C − H − N − S − ash) and may lead to overestimation of O content (Budai et al., 2013). The O/C ratio does not distinguish well between the high-ash biochars such as those produced from poultry manure compared to woody biochars even when the O/C ratios are corrected for carbonates (Enders et al., 2012).

3.1.3. Van Krevelen diagram

Van Krevelen diagram, which plots H/C against O/C, is originally used to provide clear and visual indication for the origin and maturity of petroleum and coal. It is now widely applied for biochar characterization to demonstrate the evolution of biomass components during thermal treatment. In fact, the limit on both ratios O/C_{org} (<0.4) and H/C_{org} (<0.7) required by EBC seems more like the application of Van Krevelen diagram for biochar characterization.

The change of ratios of H/C and O/C in biochar can be used to indicate the possible chemical reaction paths during the production of biochar. The progressive decrease in ratios of H/C and O/C with temperature denotes the trajectory associated with dehydration reactions (Keiluweit et al., 2010). H/C and O/C correlates closely to each other. For example, the relationships of "$H/C = 2.281 * O/C + 0.151$ ($n = 207$, $R^2 = 0.873$)" and "$H/C = 2.512 * O/C + 0.0804$ ($n = 32$, $R^2 = 0.902$)" were obtained by Klasson (2017) and Enders et al. (2012), respectively. In a recent review, Aller (2016) summarized the H/C and O/C ratios of biochar from various feedstocks and found out that except hydrochar (with H/C > 0.7) and biochar from algae (with H/C > 0.7 and O/C > 0.4), almost all other biochars can meet the requirement of IBI or EBC in terms of H/C and O/C ratios, although few biochars from cellulose-rich feedstocks and manure/waste may fail (Fig. 1).

3.2. C structure analysis by instrumental methods

Aromatic carbon structure such as aromaticity, which is the degree of poly-condensation of materials such as biochar, shows the carbonization extent of feedstock during thermal treatment. Whereas, degree of aromatic condensation is a similar property defined as the size and purity of the aromatic domain as opposed to the proportion of aromatic carbon. Strong relationships between biochar C stability (C mineralization rate) and the initial proportion of aromatic C/nonaromatic C or degree of aromatic condensation in biochar were found in many studies (Table S1). These relationships support the idea of analyzing the aromaticity and/or degree of aromatic condensation for the prediction of biochar C stability in soil. The aromaticity and degree of aromatic condensation may be qualified or even quantified by approaches detailed as follow.

3.2.1. Nuclear magnetic resonance (NMR) analysis

Solid-state ^{13}C NMR is very powerful for investigating relative small aromatic structures in biochars produced at lower temperature with lower crystallinity (Camps-arbestain et al., 2017). It is used for aromaticity measurement through estimating average aromatic cluster size using dipolar dephasing to differentiate between protonated and non-protonated aryl-C (Nguyen et al., 2010). Its utilization for aromatic condensation determination, on the other hand, depends on the principle that ring currents, which is measured using ^{13}C-labelled probe molecules absorbed to biochar, increase in strength with increasing aromatic condensation (Wiedemeier et al., 2015a).

The aromaticity and/or aromatic condensation of biochar analyzed using NMR correlated negatively with labile carbon content in biochar (Camps-arbestain et al., 2017; Manyà et al., 2014b) and with molar ratios of H/C and O/C (Manyà et al., 2014b; Wiedemeier et al., 2015a); but positively correlated with the MRT of biochar in the soil (Camps-arbestain et al., 2017; Manyà et al., 2014b). A linear correlation can be found between the aromatic C content analyzed by NMR and R_{50} (a recalcitrance index, detailed in Section 4.2.1) (Zhao et al., 2013).

On the other hand, the cluster sizes of aromatic C or the degree of aromatic condensation in biochar vary significantly between biochars independent of aromaticity. It may be more useful for biochar stability assessment than aromaticity. The degree of aromatic condensation, measured as the chemical shift of $^{13}C_{benzene}$ sorbed to biochar ($\Delta\delta$, $\Delta\delta = \delta_{sorbed\ benzene} - \delta_{neat\ benzene}$), becomes increasingly negative as the ring currents of larger and more condensed aromatic structures (with high ring numbers) increase in strength. The sizes estimated from quantitative NMR spectral analysis increase from 8 carbons (or 1–2 rings) in 300 °C char, to 18 (~4–5 rings), 40 (~13 rings), 64 (~22–23 rings), and 76 (27 rings) carbons in 400 °C, 500 °C, 600 °C, and 700 °C chars, respectively (Cao et al., 2012). More importantly, the C mineralization results from a long-term (5 years) laboratory incubation experiment conducted on biochars show that strong correlations can be found between modelled MRT and the initial proportion of nonaromatic C [$MRT = 1682 * (\text{nonaromatic C content})^{-0.696}$, $R^2 = 0.940$] and degree of aromatic condensation [$MRT = 148 * e^{1.144*(-\Delta\delta)}$, $R^2 = 0.953$] in biochar analyzed by NMR (Fig. 2) (B.P. Singh et al., 2012).

NMR clearly provides very useful characterization of biochars for predicting biochar stability. However, the wide variation in NMR equipment may further lead to the variation in C structure determination. Comparisons between results determined by different NMR equipment may lead to big difference (Camps-arbestain et al., 2017). The establishment of a set of standard biochar samples that can be made widely

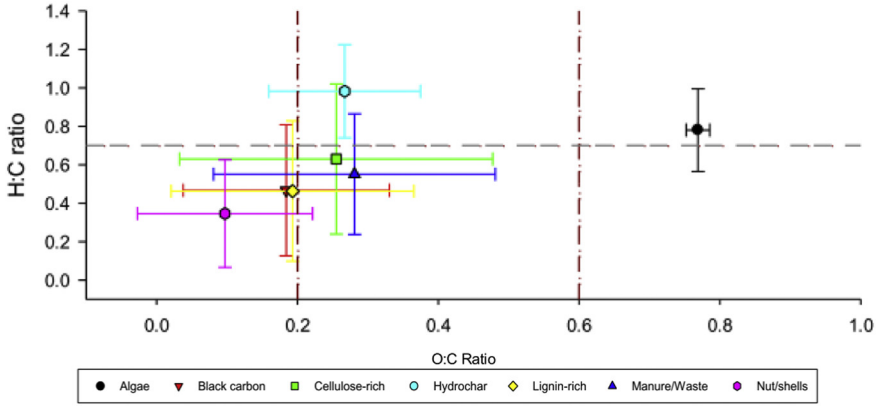

Fig. 1. Van Krevelen diagram for biochar from different feedstocks and hydrochar. Reprinted from Aller (2016).

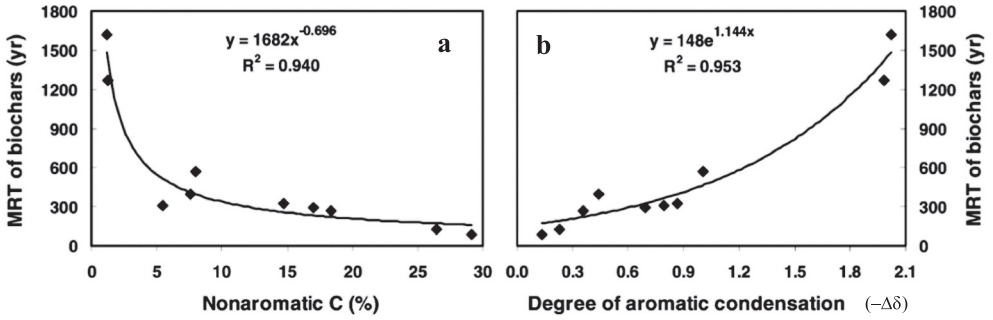

Fig. 2. Relationships between mean residence time (MRT) of biochar C (using the 5-year mineralization data) and nonaromatic C proportion (a)/degree of aromatic condensation (b) determined by ^{13}C CP NMR. Reprinted from B.P. Singh et al. (2012).

available can reduce the differences to some extent. In addition, aromatic condensation measurement may have higher applicability, but needs further more tests and inter-laboratory comparison studies.

3.2.2. X-ray diffraction (XRD) analysis

Three-dimensional information such as crystallite size, aromaticity, interlayer spacing, and other properties of carbonaceous materials such as biochar can be obtained from XRD analysis, which is advantageous for biochar with high crystallinity (Lehmann and Joseph, 2015).

XRD spectra may also be used to assess the aromaticity and aromatic condensation degree of biochar. The peak in the low angle region of X-ray intensity curve is resolved into two bands which reflect the aromatic and saturated structures, respectively, and the resulted difference can be used to assess the aromaticity of coal char (Lu et al., 2000). The aromaticity value positively related to pyrolysis temperature and increased from 58 to 72% for the selected coals to 75–82% after being treated at 1200 °C (Lu et al., 2000). Sizes of turbostratic crystallites estimated in wood and festuca grass biochars, increased from ~49 rings (19.3 Å) in 500 °C char to ~54 rings (20.4 Å) in 700 °C char, and from ~21 rings (13.8 Å) in 500 °C char to ~106 rings (28.5 Å) in 700 °C char, respectively (Keiluweit et al., 2010; Lehmann and Joseph, 2015).

3.2.3. Near-edge X-ray absorption fine structure (NEXAFS)

NEXAFS spectroscopy has been tried to estimate biochar aromaticity through spectral deconvolution of the functional group distribution as percentage of total C of the material (Heymann et al., 2011). Peak near 285.0 eV can be unambiguously assigned to double carbon–carbon (C═C) bonds without hetero-atoms as nearest neighbors (Liang et al., 2008). Bulk NEXAFS analysis of biochars quantified biochar with a total aromaticity of ~40% (Heymann et al., 2011). NEXAFS has been used by several other researchers to study the aromaticity and the degree of aromatic condensation of biochar (Keiluweit et al., 2010; Singh et al., 2014; Wiedemeier et al., 2015a). Degree of aromatic condensation results is barely consistent with those from NMR (Wiedemeier et al., 2015a). The failure for the estimation of aromatic carbon structure by simple indices derived from NEXAFS spectra may be explained by the fact that resonances in NEXAFS are derived from the entire electronic structure of the char rather than exclusively from specific functional groups.

3.2.4. X-ray photon spectroscopy (XPS)

Information about the ratio of unoxidized carbon to oxidized carbon on the surface as well as the evaluation of the relative proportions of oxygen-containing chemical groups can be obtained by XPS spectra analysis. The assignment of binding energy of C1s and O1s can be used to fractionate the functional groups. The change in O-containing carbon groups from XPS may probably refer to the short-term stability of biochar. The relative content of aromatic C—H analyzed by XPS can be used to assess biochar stability (Liang et al., 2008; Yang et al., 2016). In addition, elemental molar ratio such as O/C can be analyzed by XPS and the ratio may be indicative of biochar stability. However, the O/C values should be used after at least the correction of inorganic O, and the difference between the corrected and uncorrected can be notable (Camps-arbestain et al., 2017).

3.2.5. Fourier transform infrared spectroscopy (FTIR)

FTIR is a more widely used technique than XPS for functional groups analysis (generally as a qualification method). The application of FTIR for biochar stability analysis is based on the analysis of the carbon chemical functional groups. Specifically, the analysis is focused on the reduction/loss of O-containing functional groups and aliphatic C—H in comparison to the incremental aromatic C—H and C═C groups (Keiluweit et al., 2010; Knicker et al., 2007). The quantification of O-containing functional groups can be obtained through Boehm titration along with XPS analysis to confirm the deduction made by FTIR analysis (Boehm, 2002, 1994; Leng et al., 2015a, 2015b).

Recently, a novel technique, FTIR-microscopy, has been used to map the distribution of C forms (such as aromatic C) in entire microaggregates from a C-poor soil with/without biochar amendment and it provided a semi-qualitative information of the functionalities (Hernandez-Soriano et al., 2016). The microscopy gives a visual illustration of the different functionalities distributed in the aggregate. The map serves as fingerprints of the main molecular structures present in the biochar amended soil.

3.2.6. Infrared diffuse reflectance spectroscopy in the near- or mid-infrared spectral range (NIRS/MIRS)

Soil C content determination by NIRS and MIRS has been extensively developed in agriculture area (Bellon-Maurel and McBratney, 2011). C content in biochar can also be measured by NIRS/MIRS and it is an easy way to get detailed information about the transformations of biomass components between biochars by comparing the relative intensities of the different bands (Budai et al., 2017). Good estimations of fixed carbon (FC), volatile matter (VM) and gravimetric yield for *eucalyptus* charcoals by using NIRS (Andrade et al., 2012) and of ash, VM, FC content and calorific value for biochar produced from cedar wood, pine wood and cotton stalks (Yang and Sheng, 2012) were achieved. Kusumo et al. (2014) tried to apply NIRS for assessing stability of biochar ($n = 25$) by predicting aromatic C, FC, or atomic H/C_{org} ratio. This method is effective when accompanied by the help of accurate calibration models developed in ref. (Kusumo et al., 2014). In another study, aromaticity ratio (%) of biochars as indicated by the peak areas ratio of aromatic/(lignin + aliphatic) were obtained by using MIRS (Wiedemeier et al., 2015a). However, these assessments are generally qualitative and more research and fine tuning with respect to infrared band selection and spectral data analysis would be needed.

3.3. C structure analysis by molecular markers

Molecular markers obtained from different analysis methods can indicate the carbon structures of biochar materials which relate closely to biochar stability.

3.3.1. Polycyclic aromatic hydrocarbons (PAHs)

PAHs are possible molecular markers for stable C in biochar (Wiedemeier et al., 2015b; Wurster et al., 2013). PAHs have been used by several researchers for assessing biochar stability, but with few successes (Keiluweit et al., 2012; Wiedemeier et al., 2015b). Since the larger and non-extractable sheets stable biochar C cannot be extracted and analyzed chromatographically. Biochar produced at high HTT (i.e., HTT ≥ 600 °C) minimizes concentrations of extractable PAHs due possibly to the volatilization of the amorphous phases (which can experience condensation to produce larger and non-extractable sheets) and/or the strong sorptive retention by the more condensed biochar phases (Keiluweit et al., 2012).

3.3.2. Benzene polycarboxylic acids (BPCA)

BPCA method has been developed as a widely used marker in the last two decades for quantifying the black carbon component in charcoal, soil and sediment. It quantifies the abundant polycyclic structures which have larger and more complex than PAHs and cannot be quantified directly as polymers using chromatographic methods (Brodowski et al., 2005; Glaser et al., 1998). In BPCA method, these structures are digested and broken down into individual BPCAs amenable to gas or liquid chromatography (Camps-arbestain et al., 2017; Lehmann and Joseph, 2015). The quantified BPCAs can then be used as molecular markers to indicate the stability of biochar by the relative proportions of individual BPCA monomers or 'BPCA pattern': single-ring aromatic molecules with different degree of carboxylation, i.e., B3-, B4-, B5- and B6-CA represent BPCA with three, four, five and six carboxylic groups, respectively (Camps-arbestain et al., 2017). 'BPCA pattern' reflects the size of the original polycyclic structures. The proportion of BPCA normalized to organic carbon (total BPCA/TOC) and the ratio of individual BPCA monomers to the total BPCA (e.g., B6CAs/total BPCA) imply the aromaticity and the degree of aromatic condensation (the size of the aromatic clusters of the biochar), respectively (Camps-arbestain et al., 2017; Kusumo et al., 2014).

McBeath et al. (2011) found close correlation between total BPCA-C yield (g/kg TOC) and NMR-determined charcoal aromaticity. However, at HTT > 700 °C, total BPCA-C (g/kg TOC) values began to decrease because of the larger condensed aromatic structures that are resistant to acid oxidation, while the NMR aromaticity remained still high (McBeath et al., 2011). Interestingly, general correlation between the relative proportion of B6CA and Δδ from NMR (which denotes the degree of aromatic condensation) was observed (McBeath et al., 2011). The ratio of B6CA to total BPCA may be used along with H/C and O/C ratios to confirm the condensation extent of biochar. The calculation of cluster sizes of biochars based on B6CA/BPCA was also tested recently, and the size shows an incremental trend at HTT > 500 °C, but size for biochars produced at HTT < 500 °C stays steady (Budai et al., 2017). Additionally, this method does not really quantitate all stable C presents in the sample, with a maximum estimation of only ~25% of the total stable C which can be recovered as BPCA monomers (Camps-arbestain et al., 2017). The method of simply multiplying stable C BPCA values by a factor (e.g., 2.27 (Glaser et al., 1998)) for representing the total stable C may be inapplicable for most biochars.

3.3.3. Lipid analysis

The total lipid content in biochar may be indicative of biochar aromaticity, and the decreasing trend of the lipid content can indirectly indicate the incremental aromaticity (Wiedemeier et al., 2015a, 2015b). As HTT increases to higher temperatures, plant-derived lipids would be decomposed gradually to some small molecules, which could combine afterward to form larger molecules, whose extractability is limited. Indeed, the total lipid was found to have high extractability at low HTT, and low extractability at HTT > 500 °C (Wiedemeier et al., 2015a), making simple lipid extraction a potential proxy for aromaticity. However, the extractability remained quite stable at >500 °C and the low extractability was found for several samples at very low HTT (<300 °C) (Wiedemeier et al., 2015a). Lipids may not be a universal marker for aromaticity of biochar.

3.3.4. n-Alkanes

n-Alkanes is also a possible marker for biochar stability for a few cases. The decrease of average chain length of alkanes due to cracking of carbon bonds with increasing HTT may serve as an indirect indicator of increasing aromaticity. Plant-derived long chain (>25 C atoms) alkanes would degrade and short chain (<25 C atoms) aliphatic side chains of other lipids become increasingly significant with increasing HTT (Wiedemeier et al., 2015a; Wiesenberg et al., 2009). Although pronounced decrease of average chain length between 200 and 600 °C was observed, pyrolysis method or starting material (wood vs. grass) has dramatic influence with the scatter data, suggesting careful calibration requirements for aromaticity measurement (Wiedemeier et al., 2015a).

3.3.5. Pyrolysis-GC–MS (Py-GC–MS)

Py-GC–MS is an analytical pyrolysis technique which combines inert thermal degradation (pyrolysis) and prompt and real-time analysis (by GC–MS) of the resultant vapor and gas products from pyrolysis of the sample such as biochar. The pyrolysis conditions of Py-GC–MS is generally harsher (e.g., pyrolysis temperature of 900 °C) than those used for production of biochar in order to produce molecular markers from biochar for detection by GC–MS. Py-GC–MS provides C structure information for biochar by the molecular markers (Kaal et al., 2012b). Py-GC–MS results can be treated as pyrolysis fingerprints (pyrolysates) of the biochar, which can be used to elucidate chemical compositions of biochar and the degree of thermochemical conversion of biochar. For example, benzofuran is a marker of cellulose; polysaccharides such as furaldehyde and furfuryl alcohol are markers of holocellulose; phenols and guaiacols are markers of lignin; naphthalene is a marker of polycondensed aromatic structures (Conti et al., 2014). The proportions of labile and stable structures could then be estimated and used for the estimation of biochar stability and the degradation behavior after soil application.

Py–GC–MS data such as relative abundance ratios of toluene, *m*/*p*-xylene and benzofuran with naphthalene of biochars were directly correlated (R > 0.94) with H/C ratios (n = 27 with H/C ranging from 0.4 to 0.8), indicating their possibilities as indices of the charring intensity (Conti et al., 2014). High correlations between Py-GC–MS results and ratio of H/C were also found by several researches (Conti et al., 2016, 2014). The pyrolysis fingerprints of biochars are affected by soil properties and microbial activities during incubation experiments. For example, loss of phenols (marker of lignin) and polysaccharides (hemicellulose) from the pyrolysis fingerprints was reported for tropical wood charcoal after incubation with microbial inoculation (Leal, 2015).

3.3.5.1. Thermal stability indices (TSI). *TSI* obtained from Py-GC–MS can be used as an index for assessment of biochar stability. Thermal stability index of an individual pyrolysis component (TSI_p) can be calculated depending on Principal Components Analysis and rescaled to 0–100 (a dimensionless proxy). Then *TSI* of the biochar (TSI_b) can be obtained by multiplying the relative abundance of each pyrolysis component with its corresponding TSI_p (Eq. (1)) (Suárez-Abelenda et al., 2017). The sum obtained is then divided by 100 to scale TSI_b between 0 and 100. The calculation can be accomplished by the following equation. The TSI_p is exponentially correlated well to ratios of benzene/toluene, naphthalene/C_1-naphthalenes and stable polycyclic aromatic C/TOC (Suárez-Abelenda et al., 2017).

$$TSI_b = \sum_{i}^{n} (RP\%_i * TSI_{pi})/100 \quad (1)$$

where TSI_{pi} and $RP\%_i$ are the thermal stability index and the relative

proportion of an individual pyrolysis component (i), respectively. n is the number of components detected by Py-GC–MS.

The newly developed TSI_p may be treated as biochar stability indicator as it may control the mineralization behavior of biochar in field implementation. However, the value for biochar after its addition to soil is still unclear. Additionally, Py-GC–MS data may not be very reliable for highly carbonized biochars due to the barely detectable peaks in the pyrolysates (Calvelo Pereira et al., 2011; Conti et al., 2016). Large polyaromatic clusters with high thermal stability in biochars produced at higher temperatures have very limited "pyrolysability" during Py-GC–MS and thermally assisted hydrolysis or methylation–GC–MS may be an alternative to obtain more information of highly thermal-stable fractions in biochars (Kaal et al., 2012a).

3.3.6. HydroPyrolysis-GC–MS (HyPy-GC–MS)

HyPy, a pyrolytic process carried out at high pressure in hydrogen atmosphere in the presence of catalyst, has been used with combination of GC–MS for quantification of black carbon and biochar in environment such as in soil. HyPy-GC–MS is more powerful than Py-GC–MS and can make the analysis of molecular markers more robust. By quantifying the contents of labile and stable fractions of biochar, HyPy-GC–MS is very useful to assess the stability of biochar. The highly stable portion of the biochar from HyPy (BC_{HyPy}) (Rombolà et al., 2016) or stable polycyclic aromatic carbon (SPAC) pool (McBeath et al., 2015) are composed of highly condensed aromatic clusters commonly with fused rings >7. They can be quantified by elemental analysis after removing all labile organic matter (including non-BC_{HyPy} composed of aromatic with fused rings <7 which is semi-labile and labile fractions) (Rombolà et al., 2016). The BC_{HyPy} (or SPAC) is believed to be resistant to mineralization on centennial timescales, while non-BC_{HyPy} is less permanent and is susceptible to biological and chemical degradation and may likely be stable on timescales of years to decades (McBeath et al., 2015; Rombolà et al., 2016). BC_{HyPy} contents showed very strong inverse correlation with the molar H/C ratios of biochars ($R = -0.99$), which means that BC_{HyPy} contents could be used for the assessment of biochar stability (Rombolà et al., 2016).

3.4. C structure analysis by He pycnometry

Skeletal density measurement by He (helium) pycnometry represents a physical, simple, and completely independent approach for aromatic carbon structure analysis. He can penetrate the smallest of pores (0.1–0.2 nm open pores) and reflect the density of the C skeleton of the char samples, indirectly indicating C condensation (Wiedemeier et al., 2015a). A rather linear correlation between degree of aromatic condensation and skeletal density was found from 300 °C up to the highest measured HTT (1000 °C) (Wiedemeier et al., 2015a). The indirect skeletal density measurement as an indicator for aromatic condensation appears to reproduce quite well the main trend observed from the ratio of individual BPCA monomers to the total BPCA (e.g., B6CAs/total BPCA), while the NMR chemical shift of $^{13}C_{benzene}$ sorbed to biochar ($-\Delta\delta$) (Wiedemeier et al., 2015a). Due to the much lower cost, simpler procedure and shorter analysis time, skeletal density measurement may be developed as a promising index for aromatic condensation assessment. However, only limited studies were devoted in this area.

4. Biochar stability assessment by analyzing labile/stable biochar C

4.1. Proximate analysis

4.1.1. Fixed carbon (FC) or volatile matter (VM)

FC is closely related to stable C content. The FC yield of biochar shows biochar's potential as carbon negative material from the environmental point of view; higher yield means its higher potential as a climate change mitigation tool (Brassard et al., 2016). FC increases with the incremental pyrolysis temperature, and it may be used as biochar stability proxy. It was found positively correlated with aromatic C content (analyzed by NMR) (Manyà et al., 2014b) and with stable C content (analyzed by H_2O_2 oxidation) (Crombie et al., 2013), but negatively with O/C (Spokas, 2010).

Likewise, VM, which has close relationship with labile C, may also indicative of biochar stability. It does not necessarily constitute a property correlated with the chemical composition or structure of the biochar, but it contributes greatly to laboratory incubations because of the short-term effect on microbial activity (Zimmerman, 2010). VM is correlated positively with mineralizable C content obtained from incubation (Zimmerman, 2010) and with O/C molar ratio (Aller, 2016; Spokas, 2010), but negatively with stable C content as determined by H_2O_2 oxidation (Crombie et al., 2013).

Since FC and VM are values as percentage of total biochar and the ash yield varied dramatically between different feedstocks, the comparisons between FC or VM values of biochars from different feedstocks would probably fail to provide accurate stability information. Based on the VM content differences between various biomass and between biochars from different biomass, new classification expanding the concept by Spokas (2010) was proposed by the combination of volatile matter (ash-free) and O/C_{org} or H/C_{org} ratios for the assessment of biochar stability (Enders et al., 2012): VM > 80% may indicate biochars with no C sequestration value; VM < 80% and $O/C_{org} > 0.2$ or $H/C_{org} > 0.4$ may indicate moderate sequestration ability; VM < 80% and $O/C_{org} < 0.2$ or $H/C_{org} < 0.4$ may indicate high C sequestration potential. However, this classification method was not fully justified and verified.

4.1.2. FC and VM

Combination of FC and VM gives more accurate assessment for biochar stability. H/C and O/C molar ratios of biochars (n = 207) can be estimated from VM and FC by the expressions: $H/C = 0.379 * VM/FC + 0.251$ ($R^2 = 0.725$) and $O/C = 0.188 * VM/FC + 0.035$ ($R^2 = 0.857$) (Klasson, 2017). By using these correlations to classify the biochar (n = 207) according to the values required for classification by IBI ($H/C_{org} < 0.7$) and EBC ($H/C_{org} < 0.7$ and $O/C_{org} < 0.4$), about 16–23% of the biochars (mainly biochar produced at HTT < 400 °C) were misclassified. Only 5 biochars for EBC and 8 for IBI was misclassified when the correlations were used for biochar produced at ≥400 °C, which proved high accuracy of these equations in terms of classifying the selected biochar (Klasson, 2017). By relating VM/FC to the stability of biochar as proposed by Spokas (2010), VM/FC ratio of <0.88 (reflecting O/C < 0.2) can predict a biochar with a half-life of >1000 y, while 0.88 < VM/FC < 3.0 (reflecting 0.2 < O/C < 0.6) can predict a half-life of 100–1000 y (Klasson, 2017). VM/FC was also found negatively correlated with stable C content (analyzed by H_2O_2 oxidation) (Klasson, 2017).

On the other hand, the thermo-degradable fraction (equals to VM/(VM + FC)) can be used to provide stability information for the biochars; it is negatively related to stable C content (analyzed by $K_2Cr_2O_7$ oxidation) (Calvelo Pereira et al., 2011) and to aromatic C content (analyzed by NMR) (Brewer et al., 2011), but positively to O/C (Calvelo Pereira et al., 2011).

However, proximate analysis which is performed at 900 °C for determination of VM and 750 °C for ash determination within extended periods of time, may lead to an inflated estimation of FC (calculated by difference based on ash and volatile yields) because of underestimating ash content due to the volatilization of ash components such as carbonates and P-, K- and S-compounds (Crombie et al., 2013; Enders et al., 2012). Other testing conditions such as furnace reheating and heating rate may also be problematic for replicability (Enders et al., 2012).

4.2. Thermal degradation

Thermal stability can be used to determine biochar stability by assessing the fraction of C that can endure the thermal oxidation and

thus obtaining the amount or the relative stability of labile or stable C in biochar.

4.2.1. Temperature-programmed oxidation (TPO)

TPO indices such as oxidative onset temperature and oxidative induction time determined by thermogravimetry (TG)/thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC) are widely used to assess the oxidative stability of materials such as biodiesel. During TPO, sample is oxidized in oxygen or oxygen-containing atmosphere to accelerate the decomposition. It is good for biochar stability measurement since less alteration would happen to the sample under lower temperature.

The weight loss characteristics observed from TG/DTG (-DSC) curves can be used to assess the relative stability of a biochar: degradation range of 30–200 °C reflects the presence of volatile organic C, 200–380 °C of labile organic C (predominantly cellulose such as aliphatic C and carbohydrates), 380–475 °C of recalcitrant organic C (predominantly lignin and recalcitrant C such as aromatic C), 475–600 °C of refractory organic C (polycondensed forms of lipids and aromatic C), and 600–1000 °C of inorganic C (carbonates), respectively (Leng et al., 2018c; Zornoza et al., 2016). Peak temperature is the most reliable attribute to characterize the thermal oxidative stability. During DSC analysis in synthetic air of wood, charred wood, charcoal, soot, and graphite demonstrated that peak temperatures increased in sequence from wood to graphite (Leifeld, 2007). The stability mechanisms, however, seem different. The oxidative stability of these materials, after comparing with NMR data, is believed to be controlled more by the degree of order (crystallinity) rather than by the aromaticity (Leifeld, 2007).

4.2.2. Recalcitrance index (R_{50})

Recalcitrance index (R_{50}), is also an TPO index and it was proposed by Harvey et al. (2012) to specifically evaluate the thermal oxidative stability of biochar. R_{50} is a relative stability as compared to graphite. It is calculated by dividing $T_{50,x}$, which is the temperature value corresponding to 50% oxidation/volatilization of biochar, by $T_{50,\ graphite}$, an external standardization factor (T_{50} = 885 °C) (Eq. (2)). $T_{50,x}$ and $T_{50,\ graphite}$ are obtained directly from TG thermograms after correction of water and ash content with method reported in ref. (Harvey et al., 2012). The R_{50} index for graphite is the highest (R_{50} = 1), while those of biochars (n = 59) produced under different conditions were in the range of 0.37–0.61, with values positively correlated with HTT (Harvey et al., 2012). A strong negative exponential-type relationship between biochar degradability (abiotic + biotic) during 1-year incubation and thermal oxidation recalcitrance during thermal degradation was built (Fig. 3) (Harvey et al., 2012). Based on this relationship, R_{50} index classification of biochar was proposed: Class A with $R_{50} \geq 0.70$ has the highest stability; Class B with $0.50 \leq R_{50} < 0.70$ has lower stability but much higher than Class C with $R_{50} < 0.50$ which is comparable with uncharred plant biomass (Harvey et al., 2012).

$$R_{50} = T_{50,x}/T_{50,graphite} \quad (2)$$

R_{50} has been used by several researchers to characterize biochar. R_{50} value ranges of 0.45–0.60 and 0.41–0.83 were observed in refs. Windeatt et al. (2014) and Zhao et al. (2013), respectively. Modification for R_{50} assessment method was studied with a new index "gained stability" (GS) being proposed and calculated by Eq. (3) to interpret the biochar stability (Gómez et al., 2016). Strong correlation (R = 0.97) was observed between "gained stability" index and the accelerated aging test results obtained by the method developed by Cross and Sohi (2013).

$$GS = (R_{50,X} - R_{50,CELL})/(R_{50,PCELL} - R_{50,CELL}) \quad (3)$$

where $R_{50,\ X}$, $R_{50,\ CELL}$ and $R_{50,\ PCELL}$ are the R_{50} values of biochar, cellulose and cellulose char produced at HTT 750 °C for 1 h, respectively.

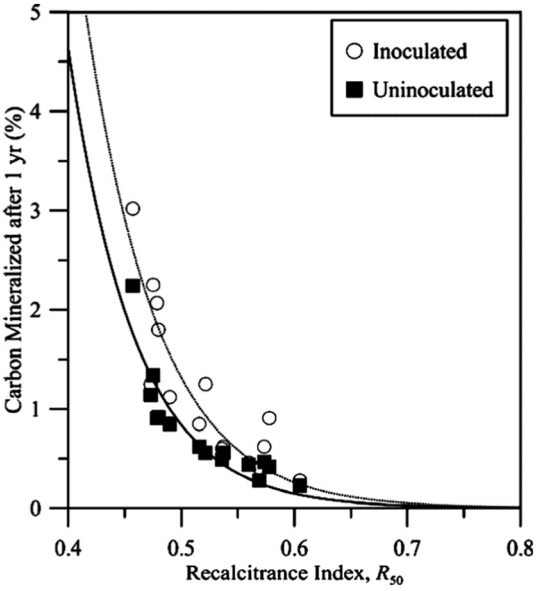

Fig. 3. Relationship between biochar degradability and thermal recalcitrance R_{50}. Reprinted from Harvey et al. (2012).

4.3. Chemically accelerated aging

Chemically accelerated aging applies chemicals to remove the labile C in biochar by chemical reactions such as oxidation and thus leaving the stable C (Table S2).

4.3.1. H_2O_2- and heat-assisted oxidation (Edinburgh stability tool)

Cross and Sohi (2013) developed an accelerated aging method (also called Edinburgh stability tool) for the simulation of oxidative nature of biochar degradation in soil, in which accelerated oxidation is conducted by adding 5% hydrogen peroxide (H_2O_2) to biochar sample and heat at 80 °C for 2 days until the solution dries out. Biochar carbon stability (Æ), which is defined as the proportion of initial carbon remaining after oxidation treatment, can be determined by the residual stable carbon mass in biochar residue after oxidation (as percentage of the total carbon mass in original biochar) (Eq. (4)). The carbon stability of biochars from different feedstocks obtained by this method shows value between 60 and 80% (Cross and Sohi, 2013).

$$\hat{A}\hat{0} = B_r * B_rC * 100\%/(B_t * B_tC) \quad (4)$$

where B_t and B_r are the residual and total biochars mass before and after oxidation; B_tC and B_rC are the C content in residual and total biochars mass before and after oxidation.

Further comparing the mass loss after oxidation of wood charcoal produced in this study to the mineralization behavior of the natural analogue (wildfire charcoal) studied in refs. Crombie et al. (2013) and Lehmann et al. (2008), a resultant exerted aging equivalent of 92 years and 187 years under mean annual temperatures of 17 °C and 7 °C was obtained by Cross and Sohi (2013). It is a pattern distinct from O/C ratio. It has the potential for quantitative calibration of the stability assessment against patterns of charcoal aging observed in the natural environment. Cross and Sohi proposed that the accelerated aging method captures the physical constraints to degradation which is not reflected in elemental ratios, e.g., the micromorphology of biochar arising from the feedstock and the compositions and physical distributions of its mineral constituents (Cross and Sohi, 2013). It is believed to be a reliable approach to quantify the stable C content in biochar (Crombie et al., 2013; Mašek et al., 2013). Strong correlations were observed between the stable C (Æ) and FC (R > 0.79), VM (R > 0.79), or O/C (R =

−0.847, $p < 0.0001$) (Crombie et al., 2013). Values obtained by this method are comparable to those obtained by R_{50} (Yang et al., 2016).

However, the estimation of the longevity of biochar in the study was based on several assumptions: the manmade charcoal is assumed to mimic the natural wildfire charcoal, and the mean residence time of the eliminated part of the charcoal by treatment with 0.01 mol of H_2O_2 is of a certain-value year (i.e., 45 years) equivalent long. Therefore, more verifications may need to be done to justify their assumptions and calibrations before this index can be widely accepted as a way for the biochar stability assessment.

4.3.2. Dichromate ($K_2Cr_2O_7$) oxidation

The chemical oxidative stability of biochar can be determined by using only chemicals without heat treatment. Chemical oxidation can be performed by using the potassium dichromate ($K_2Cr_2O_7$). It is a common approach for the quantification of black carbon in soils and sediments (Knicker et al., 2007). The consumption of $K_2Cr_2O_7$ can be determined spectrophotometrically with the mass of oxidized carbon calculated by Eq. (5). The fraction of the oxidized carbon (labile C) can then be obtained by multiplying total carbon content in biochar.

$$2K_2Cr_2O_7 + 3C + 8H_2SO_4 = 2K_2SO_4 + 2Cr_2(SO_4)_3 + 3CO_2\uparrow + 8H_2O \quad (5)$$

Carbon loss is related to aromatic substances and oxygen-containing functional groups (analyzed by infrared method), and to ratios of O/C and H/C (from elemental analysis) (Chen et al., 2016c). The correlations between potassium dichromate oxidized fraction and O/C ratio are significant (Pearson's $r = 0.948$, $n = 6$, $p < 0.05$ (Calvelo Pereira et al., 2011) and Pearson's $r = 0.9934$, $n = 5$ (Chen et al., 2016c)). Positive linear correlations were found between the percentage of C that resists acid dichromate oxidation and the de-alkylation degree of molecules detected by Py-GC–MS ($R^2 = 0.70$, $p < 0.01$ for benzene/toluene ratio; $R^2 = 0.92$, $p < 0.001$ for benzonitrile/methyl-benzonitrile ratio) (Kaal and Rumpel, 2009). $K_2Cr_2O_7$ was found to have stronger oxidizing ability to biochar samples than H_2O_2 (Xu et al., 2017). However, it is worth mentioning that the sample pool size is too small in these studies and their conclusions need more verifications.

4.3.3. Permanganate ($KMnO_4$) oxidation

Oxidation stability of biochar was also assessed by using potassium permanganate as the oxidant (Calvelo Pereira et al., 2011). The potassium permanganate oxidized fraction as per TOC correlated well to molar ratios of H/C or O/C (Calvelo Pereira et al., 2011). However, oxidized C fractions as per TOC of biochars were constantly <50 g/kg (5–46 g/kg), which were much lower than those obtained from oxidation by potassium dichromate (ranged between 180 and 545 g/kg) (Calvelo Pereira et al., 2011).

4.3.4. Other chemical aging methods

Other chemicals can be used for accelerating the biochar aging or for extracting labile biochar fractions. For example, the resistance of black carbon to acid hydrolysis was carried out by extracting the black carbon for 12 h at 105 °C using 5 M HCl and the residue can be treated as part of the recalcitrant soil organic matter pool (Rumpel et al., 2007). However, the organic carbon was less sensitive to acid extraction (carbon loss 2–15%) than to dichromate oxidation (carbon loss 24–76%) despite of the high sensitivity for organic nitrogen (Rumpel et al., 2007). Labile fraction of biochar determination by chemical extraction (e.g., hot water extraction and acid/base extraction) would likely to be underestimated and biochar stability may be overestimated (Bakshi et al., 2018). Therefore, this method may be unreliable. Indeed, results from extraction of gasification biochar (with high aromatic carbon structures) and hydrochar (contain aliphatic compounds in addition to aromatic C) show that the proportion of C remained extraction of biochar and hydrochar had no obvious difference (Naisse et al., 2013).

Additionally, aging with enzymes such as horseradish peroxidase enzymatic oxidation may also be possible for developing biochar stability assessment protocols (Fidel et al., 2017).

5. Biochar stability assessment by biochar incubation and modelling

Unlike the methods to determine the aromaticity, degree of aromatic condensation, and labile/stable C (oxidation resistance) of biochar which evaluate biochar stability indirectly, biochar incubation and modelling allows the direct assessment of biochar stability. It can give the longevity value (e.g., MRT) of the tested biochar that can persist under the test incubation conditions. Generally, this value is a calculated one based on modelling of incubation data (biochar C mineralization rate). The real biochar stability can only be obtained by incubating the biochar in the soil until it degrades completely, and the degradation duration (biochar stability) can then be recorded. However, the longevity of a biochar is so long, e.g., hundreds of years, that the recording of a real value is impossible and impractical. The longest biochar (not including charcoal) incubation experiments were reported to have lasted for only a decade (Kuzyakov et al., 2014; Weng et al., 2017). Modelling the biochar incubation data (e.g., the efflux CO_2 from degradation of biochar during incubation) to calculate a simulated degradation duration value or the average time that the biochar is present (e.g., MRT) is the practical method to make the biochar stability assessment.

Calculation of MRT is generally done firstly by fitting the biochar mineralization data (e.g., the efflux CO_2) with exponential decay models, and then by calculating the reciprocal of the decay rate (Lehmann and Joseph, 2015). One-, double-, and three-pool models have been developed and used for the data fitting depending on the number of C pools assumed in biochar, and the model equations can be seen as follow (Herath et al., 2015; Lehmann and Joseph, 2015; N. Singh et al., 2012; Wang et al., 2016; Zimmerman, 2010; Zimmerman et al., 2011).

$$C_r = \sum_{n=1}^{n} \left(C_n \times e^{-k_n \times t} \right) \quad (6)$$

$$\sum_{n=1}^{n} C_n = C_0 \quad (7)$$

where C_r and C_0 represent remaining biochar C pool at time t during incubation and initial biochar C pool, respectively. C_n means the different initial biochar C pool, and $n = 1$ means one-pool model and only one C pool is assumed ($C_1 = C_0$); $n = 2$ means double-pool model with two C

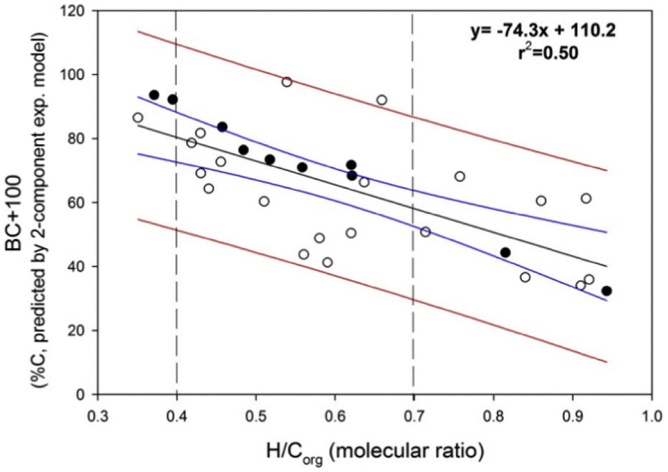

Fig. 4. Relationship between BC_{+100} and H/C_{org}. Reprinted from Budai et al. (2013).

Table 1
Advantages and disadvantages of methods based on determination of aromaticity and degree of aromatic condensation.

Methods	Advantages	Disadvantages	Comments
Ultimate analysis H/C_{org}; O/C_{org}	▪ Easy; ▪ Low cost; ▪ Closely correlated with data of incubation experiments and their modelling results.	▪ Conservative; ▪ Qualitative; ▪ Based on only several incubation experiments and their modelling results.	▪ The most widely accepted indicator for biochar stability assessment; ▪ Can be further improved by integrating more incubation experiments results.
Solid-state ^{13}C Nuclear magnetic resonance spectroscopy (NMR)	▪ Effective for quantitative assessment of aromaticity and aromatic condensation degree; ▪ Stability results highly correlate with many other methods including modelled MRT values.	▪ Expensive; ▪ Aromaticity may be insensitive ▪ Large variation between different NMR equipment.	▪ Very promising to be further developed
X-ray diffraction (XRD)	▪ Can be used for analyzing aromatic condensation degree for biochar with high crystallinity.	▪ Method not fully validated.	▪ Not sensitive for biochar produced at low temperature and needs to be further validated.
Near-edge X-ray absorption fine structure (NEXAFS)		▪ Very expensive; ▪ Method not fully validated.	▪ Not sensitive for biochar produced at low temperature and needs to be further validated.
X-ray photon spectroscopy (XPS)	▪ Can be used for aromaticity assessment.	▪ Expensive; ▪ Analyze only the functional groups on the surface; ▪ Method not fully validated.	▪ May be promising and needs to be further validated.
Mid-infrared spectroscopy (MIR)		▪ Qualitative.	▪ May be used as supplementary methods and needs to be further validated.
Fourier transform infrared spectroscopy (FTIR)	▪ Low cost.	▪ Qualitative.	▪ May be used as supplementary methods and needs to be further validated.
Benzene polycarboxylic acid (BPCA)	▪ Relatively accurate for biochar produced at low temperature.	▪ Not accurate for biochar produced at high temperature; ▪ Needs several sample treatment procedures and precise analysis.	▪ A promising method and needs further optimization.
Polycyclic aromatic hydrocarbons (PAHs)	▪ Can be used for biochar produced at low temperature.	▪ Inaccurate for biochar produced at high temperature.	
Lipid analysis		▪ Inaccurate for biochar produced at high temperature.	
n-Alkanes		▪ Inaccurate for biochar produced at high temperature.	
He pycnometry	▪ Very simple; ▪ Low cost.	▪ Method not fully validated.	▪ May be promising and needs to be further validated.
Pyrolysis-GC–MS	▪ Seems of high accuracy for biochar at low temperature.	▪ Needs several sample treatment procedures and precise analysis; ▪ May not be very reliable for highly carbonized biochars.	▪ Not sensitive for biochar produced at high temperature and needs to be further validated.
HydroPyrolysis-GC–MS	▪ Seems of high accuracy.	▪ Needs complex sample treatment procedures and precise analysis; ▪ Could be expensive.	▪ A promising method and needs further optimization.

Table 2
Advantages and disadvantages of methods based on analysis of stable/labile biochar C.

Methods	Advantages	Disadvantages	Comments
Proximate analysis Volatile matter (VM); Fixed carbon (FC); VM/FC; VM/(VM + FC)	▪ Easy; ▪ Good correlation with other indices such as ultimate analysis results and aromaticity.	▪ Depend on meta-analysis (results of other methods); ▪ Variations exist due to the different conditions used for proximate analysis.	▪ Can be used as supplementary methods.
Recalcitrance index (R_{50})	▪ Very simple; ▪ Low cost; ▪ Seems of high accuracy.	▪ Classification of R_{50} index not fully validated.	▪ Promising and needs further development and optimization.
Modified Recalcitrance index ("gained stability")	▪ May increase the accuracy of R_{50}	▪ Method needs further validation.	
Thermal stability indices (*TSI*)	▪ Seems of high accuracy.	▪ Developed based on results from Pyrolysis-GC–MS; ▪ Method needs to be validated; ▪ Need a robust database; ▪ May not be very reliable for highly carbonized biochars.	▪ Promising and needs further development and optimization.
Temperature-programmed oxidation (*TPO*)	▪ Easy; ▪ Low cost.	▪ Less accurate.	
H_2O_2 oxidation (Edinburgh stability tool)	▪ Easy; ▪ Low cost.	▪ Method needs to be further validated.	▪ May be further developed and optimized to increase the accuracy.
Potassium dichromate ($K_2Cr_2O_7$) oxidation	▪ Easy; ▪ Low cost.	▪ Method needs to be validated.	▪ May be promising and needs to be further validated.
Permanganate oxidation	▪ Easy; ▪ Low cost.	▪ Method needs to be validated.	▪ May be promising and needs to be further validated.
Hot water extraction	▪ Easy; ▪ Low cost.	▪ Inaccurate.	
Acid/base extraction	▪ Easy; ▪ Low cost.	▪ Inaccurate.	

pools; n = 3 means three-pool model with three C pools. k_n means the decay rate of each corresponding C pool.

Each decay rate can be used to calculate the MRT (MRT = $1/k_n$) of the corresponding C pool; different MRT value will be obtained due to the varied mineralization rates of different biochar C pools. One-pool model which assumes an average decay rate for all C in biochar is very likely to underestimate the MRT. Whereas, double-pool model, which assumes biochar consisting of a labile C and a stable C pools, is the most commonly used model (N. Singh et al., 2012; Wang et al., 2016; Zimmerman et al., 2011). The meta-analysis study which used double-exponential model for estimation of MRT obtained MRT values of labile (pool size 3 ± 0.6%) and recalcitrant C (pool size 97 ± 0.6%) pools to be 108 ± 196 days and 556 ± 483 years, respectively (Wang et al., 2016).

In addition to MRT, half-life time and BC_{+100} have also been used to represent biochar stability assessed from incubation and modelling. Half-life time can be obtained by multiplying MRT by the natural logarithm of 2 ($t_{1/2}$ = MRT * ln2). Whereas, BC_{+100} is the percentage of C in biochar that can remain stable for >100 years predicted from MRT, and the detailed methods to obtain BC_{+100} can be found in ref. Budai et al. (2013). BC_{+100} can be further used to correlate with biochar properties to allow easy utilization of biochar properties (e.g., proximate analysis results) as biochar stability proxies. For example, the limit lines of $H/C_{org} < 0.4$ and $0.4 < H/C_{org} < 0.7$ mean that 70% (BC_{+100} value) and 50% (BC_{+100} value) of the biochar C can remain stable in soil after 100 years, respectively (Fig. 4) (Budai et al., 2013).

6. Perspectives and conclusions

Biochar incubation and modelling is the major path in the current stage for obtaining biochar stability because the results relate directly to the persistence of biochar in soil. However, due to the time-consuming and costly disadvantages of incubation study, results of aromaticity, degree of aromatic condensation and labile/stable C of biochar would eventually be used as proxies for biochar stability assessment. Simultaneous characterization of biochar during biochar incubation is pivotal to correlate biochar properties with results from incubation and modelling. This review provides the method details that can be used for these biochar property characterizations (Tables S1 and S2). Advantages and disadvantages of each methods are summarized in Tables 1 and 2.

Based on some correlations and conservative estimation (Budai et al., 2013), H/C_{org} (<0.7) is adopted by IBI (2015), with both H/C_{org} (<0.4) and O/C_{org} (<0.7) required by EBC (2012) as the indices for biochar stability. O/C_{org} and/or H/C_{org} are used as biochar stability proxies because of their low cost, easy availability and their strong correlations with biochar mineralization (Spokas, 2010). Meanwhile, aromaticity and/or degree of aromatic condensation analyzed by other techniques such as NMR, XPS, NEXAFS, XRD and BPCA can also be indicative. However, aromaticity and degree of aromatic condensation global data set lack close relationship with incubation results. For particular, the newly developed thermal stability indices (*TSI*) characterized by Py-GC–MS was found very robust for biochar aromaticity characterization, but it needs further validation (Suárez-Abelenda et al., 2017). However, material properties of biochar such as H/C_{org} alone will not allow the prediction of its total mineralization dynamics. The use of biochar properties such as H/C_{org} as a current practical solution will at best offer only a conservative estimation that can over time be improved through more sophisticated approaches. In addition, ratios of H/C_{org} and O/C_{org} are qualitative approaches as they do not specify a strong and direct calculation relationship with the biochar real stability in soil (such as MRT from incubation).

Thermal oxidative stability indices such as R_{50} (Harvey et al., 2012) and chemical oxidation resistance from such as H_2O_2- and heat-assisted oxidation (Edinburgh stability tool) (Cross and Sohi, 2013) may be possible to be developed as biochar stability proxies. Even more commonly accessible and cost-effective measurements is the combination of volatile matter and fixed carbon obtained from proximate analyses, which were found closely related to O/C and/or H/C ratios (Klasson, 2017). These thermochemical oxidation stability evaluations allow for determining both biotic and abiotic degradation potential and may imitate the biochar degradation in soils. However, these methods are all based on the assumption that the labile C correlate closely and positively with the mineralizable C of biochar in soil. To some extent, these assumptions may seem arbitrary unless there are data available to closely correlate them in this way. For example, treatment of biochar with Edinburgh stability tool resulted in 1.7% elimination of the manmade charcoal which is inferred (based on several assumptions) to be an equivalent elimination of MRT (i.e., 45 years) (Cross and Sohi, 2013).

Over all, an appropriate proxy should be: sufficiently cost-effective; relatively rapid (ideally within hours); repeatable; robust to different biochar properties and analytical capabilities; strong and preferably linear relationship with mineralization; available in different analytical laboratories; and ideally to capture a specific chemical property rather than an operational definition.

Biochar stability assessment by different methods obtained with varied results. Normalization of the experimental results into the same scale could allow for more robust comparisons to be made between and within different experimental results from the same or different methods. Meta-analysis can then be used to interpret results from wide range of source and provide useful information. However, results from meta-analysis should also be used cautiously as there are so many co-variables in different studies (many of them were not reported) which can result in comparison of large deviation. In the future, biochar stability studies are suggested to include characterization of a minimum set of properties of the specific biochar and the environment it is applied to. Documentation of microbial available C, surface area, pore size distribution, pH, ash content, and elemental analyses as well as production conditions (HTT and residence time) and feedstock type have been recommended at minimum. Availability of standard biochar materials would boost the comparability between research methods (e.g., the use of graphite in R_{50}). Before that, characterization and contrasting of different biochars would be useful rather than one biochar studied on its own.

Although the use of biochar as a tool for climate change mitigation is still under experimental investigation, it is undeniable that biochar can play an important role in the future with simultaneous climate change mitigation, soil improvement, soil remediation, and crop productivity enhancement. However, the current available data and methods cannot yet support accurate estimation of biochar stability over time. The development of biochar stability assessment methods will promote the fast advance of biochar application for climate change mitigation.

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Appendix A. Supplementary data

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References

Aller, M.F., 2016. Biochar properties: transport, fate, and impact. Crit. Rev. Environ. Sci. Technol. 46, 1183–1296. https://doi.org/10.1080/10643389.2016.1212368.

Anca-Couce, A., 2016. Reaction mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis. Prog. Energy Combust. Sci. 53, 41–79. https://doi.org/10.1016/j.pecs.2015.10.002.

Andrade, C., Trugilho, P., Gherardi Hein, P., Lima, J., Napoli, A., 2012. Near infrared spectroscopy for estimating *Eucalyptus* charcoal properties. J. Near Infrared Spectrosc. 20, 657. https://doi.org/10.1255/jnirs.1028.

Bakshi, S., Banik, C., Laird, D.A., 2018. Quantification and characterization of chemically- and thermally-labile and recalcitrant biochar fractions. Chemosphere 194, 247–255. https://doi.org/10.1016/j.chemosphere.2017.11.151.

Bellon-Maurel, V., McBratney, A., 2011. Near-infrared (NIR) and mid-infrared (MIR) spectroscopic techniques for assessing the amount of carbon stock in soils - critical review and research perspectives. Soil Biol. Biochem. 43, 1398–1410. https://doi.org/10.1016/j.soilbio.2011.02.019.

Boehm, H.P., 1994. Some aspects of the surface chemistry. Carbon N. Y. 32, 759–769.

Boehm, H.P., 2002. Surface oxides on carbon and their analysis: a critical assessment. Carbon N. Y. 40, 145–149.

Brassard, P., Godbout, S., Raghavan, V., 2016. Soil biochar amendment as a climate change mitigation tool: key parameters and mechanisms involved. J. Environ. Manag. 181, 484–497. https://doi.org/10.1016/j.jenvman.2016.06.063.

Brewer, C.E., Unger, R., Schmidt-Rohr, K., Brown, R.C., 2011. Criteria to select biochars for field studies based on biochar chemical properties. Bioenergy Res. 4, 312–323. https://doi.org/10.1007/s12155-011-9133-7.

Brodowski, S., Rodionov, A., Haumaier, L., Glaser, B., Amelung, W., 2005. Revised black carbon assessment using benzene polycarboxylic acids. Org. Geochem. 36, 1299–1310. https://doi.org/10.1016/j.orggeochem.2005.03.011.

Bruun, E.W., Ambus, P., Egsgaard, H., Hauggaard-Nielsen, H., 2012. Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. Soil Biol. Biochem. 46, 73–79. https://doi.org/10.1016/j.soilbio.2011.11.019.

Budai, A., Zimmerman, A.R., Cowie, A.L., Webber, J.B.W., Singh, B.P., Glaser, B., Masiello, C.A., Andersson, D., Shields, F., Lehmann, J., Camps Arbestain, M., Williams, M., Sohi, S., Joseph, S., 2013. Biochar Carbon Stability Test Method: An Assessment of Methods to Determine Biochar Carbon Stability. IBI Doc. Carbon Methodol. Int. Biochar Initiat URL. www.biochar-international.org, Accessed date: 25 August 2017 (WWW Document).

Budai, A., Calucci, L., Rasse, D.P., Strand, L.T., Pengerud, A., Wiedemeier, D., Abiven, S., Forte, C., 2017. Effects of pyrolysis conditions on *Miscanthus* and corncob chars: characterization by IR, solid state NMR and BPCA analysis. J. Anal. Appl. Pyrolysis 128, 335–345. https://doi.org/10.1016/j.jaap.2017.09.017.

Calvelo Pereira, R., Kaal, J., Camps Arbestain, M., Pardo Lorenzo, R., Aitkenhead, W., Hedley, M., Macías, F., Hindmarsh, J., Maciá-Agulló, J.A., 2011. Contribution to characterisation of biochar to estimate the labile fraction of carbon. Org. Geochem. 42, 1331–1342. https://doi.org/10.1016/j.orggeochem.2011.09.002.

Camps-arbestain, M., Lehmann, J., Singh, B. (Eds.), 2017. Biochar: A Guide to Analytical Methods, 1st ed. CSIRO PUBLISHING, Boca Raton, London and New York.

Cao, X., Pignatello, J., Li, Y., Lattao, C., Campbell, M.A., Chen, N., Lesley, M.F., Mao, J., 2012. Characterization of wood chars produced at different temperatures using advanced solid-state ^{13}C NMR spectroscopic techniques. Energy Fuel 26, 5983–5991. https://doi.org/10.1021/Ef300947s.

Chen, D., Chen, X., Sun, J., Zheng, Z., Fu, K., 2016a. Pyrolysis polygeneration of pine nut shell: quality of pyrolysis products and study on the preparation of activated carbon from biochar. Bioresour. Technol. 216, 629–636. https://doi.org/10.1016/j.biortech.2016.05.107.

Chen, D., Li, Y., Cen, K., Luo, M., Li, H., Lu, B., 2016b. Pyrolysis polygeneration of poplar wood: effect of heating rate and pyrolysis temperature. Bioresour. Technol. 218, 780–788. https://doi.org/10.1016/j.biortech.2016.07.049.

Chen, D., Yu, X., Song, C., Pang, X., Huang, J., Li, Y., 2016c. Effect of pyrolysis temperature on the chemical oxidation stability of bamboo biochar. Bioresour. Technol. 218, 1303–1306. https://doi.org/10.1016/j.biortech.2016.07.112.

Cheng, C.H., Lehmann, J., Thies, J.E., Burton, S.D., 2008. Stability of black carbon in soils across a climatic gradient. J. Geophys. Res. Biogeosci. 113, 1–10. https://doi.org/10.1029/2007JG000642.

Conti, R., Rombolà, A.G., Modelli, A., Torri, C., Fabbri, D., 2014. Evaluation of the thermal and environmental stability of switchgrass biochars by Py-GC-MS. J. Anal. Appl. Pyrolysis 110, 239–247. https://doi.org/10.1016/j.jaap.2014.09.010.

Conti, R., Fabbri, D., Vassura, I., Ferroni, L., 2016. Comparison of chemical and physical indices of thermal stability of biochars from different biomass by analytical pyrolysis and thermogravimetry. J. Anal. Appl. Pyrolysis 122, 160–168. https://doi.org/10.1016/j.jaap.2016.10.003.

Crombie, K., Mašek, O., Sohi, S.P., Brownsort, P., Cross, A., 2013. The effect of pyrolysis conditions on biochar stability as determined by three methods. GCB Bioenergy 5, 122–131. https://doi.org/10.1111/gcbb.12030.

Cross, A., Sohi, S.P., 2013. A method for screening the relative long-term stability of biochar. GCB Bioenergy 5, 215–220. https://doi.org/10.1111/gcbb.12035.

EBC, 2012. European Biochar Certificate - Guidelines for a Sustainable Production of Biochar. European Biochar Foundation (EBC), Arbaz, Switzerland http://www.european-biochar.org/en/download 10.13140/RG.2.1.4658.7043 (Version 6.3E of 14th August 2017).

Enders, A., Hanley, K., Whitman, T., Joseph, S., Lehmann, J., 2012. Characterization of biochars to evaluate recalcitrance and agronomic performance. Bioresour. Technol. 114, 644–653. https://doi.org/10.1016/j.biortech.2012.03.022.

Fang, Y., Singh, B., Singh, B.P., 2015. Effect of temperature on biochar priming effects and its stability in soils. Soil Biol. Biochem. 80, 136–145. https://doi.org/10.1016/j.soilbio.2014.10.006.

Fidel, R.B., Laird, D.A., Parkin, T.B., 2017. Impact of biochar organic and inorganic carbon on soil CO and NO emissions. J. Environ. Qual. 46, 505. https://doi.org/10.2134/jeq2016.09.0369.

Glaser, B., Haumaier, L., Guggenberger, G., Zech, W., 1998. Black carbon in soils: the use of benzenecarboxylic acids as apecific markers. Org. Geochem. 29, 811–819.

Gómez, N., Rosas, J.G., Singh, S., Ross, A.B., Sánchez, M.E., Cara, J., 2016. Development of a gained stability index for describing biochar stability: relation of high recalcitrance index (R50) with accelerated ageing tests. J. Anal. Appl. Pyrolysis 120, 37–44. https://doi.org/10.1016/j.jaap.2016.04.007.

Harvey, O.R., Kuo, L., Zimmerman, A.R., Louchouarn, P., Amonette, J.E., Herbert, B.E., 2012. An index-based approach to assessing recalcitrance and soil carbon sequestration potential of engineered black carbons (biochars). Environ. Sci. Technol. 46, 1415–1421. https://doi.org/10.1021/es2040398.

Herath, H.M.S.K., Camps-Arbestain, M., Hedley, M.J., Kirschbaum, M.U.F., Wang, T., van Hale, R., 2015. Experimental evidence for sequestering C with biochar by avoidance of CO_2 emissions from original feedstock and protection of native soil organic matter. GCB Bioenergy 7, 512–526. https://doi.org/10.1111/gcbb.12183.

Hernandez-Soriano, M.C., Kerré, B., Kopittke, P.M., Horemans, B., Smolders, E., Spokas, K.A., Atkinson, C., Fitzgerald, J., Hipps, N., Lehmann, J., Criscuoli, I., Steinbeiss, S., Gleixner, G., Antonietti, M., Lehmann, J., Borchard, N., Hernandez-Soriano, M.C., Farrell, M., Lehmann, J., Gaunt, J., Rondon, M., Harvey, O.R., Joseph, S.D., Liang, B., Cross, A., Sohi, S.P., Pignatello, J.J., Kwon, S., Lu, Y.F., Pignatello, J.J., Jianming, X., Donald, L.S., Stewart, C.E., Zheng, J., Botte, J., Cotrufo, M.F., Bruun, E.W., Ambus, P., Egsgaard, H., Hauggaard-Nielsen, H., Smith, J.L., Collins, H.P., Bailey, V.L., Brodowski, S., John, B., Flessa, H., Amelung, W., Herath, H.M.S.K., Camps-Arbestain, M., Hedley, M., Qayyum, M., Steffens, D., Reisenauer, H., Schubert, S., Lehmann, J., Czimczik, C., Laird, D., Sohi, S., J, L., S, J., Chia, C.H., Herath, H.M.S.K., Camps-Arbestain, M., Hedley, M., Van Hale, R., Kaal, J., Falconer, R.E., Verchot, L.V., Dutaur, L., Shepherd, K.D., Albrecht, A., Kimetu, J., Lehmann, J., Lehmann, J., Solomon, D., Singh, B., Markus, G., Lehmann, J., Kinyangi, J., Solomon, D., Solomon, D., Wan, J., Tyliszczak, T., Tokunaga, T.K., Fellman, J.B., Miller, M.P., Cory, R.M., D'Amore, D.V., White, D., Ohno, T., He, Z., Tazisong, I.A., Senwo, Z.N., Kellerman, A.M., Kothawala, D.N., Dittmar, T., Tranvik, L.J., Fellman, J.B., Hood, E., Spencer, R.G.M., Xue, S., Zhao, Q., Wei, L., Song, Y., Tie, M., Borisover, M., Lordian, A., Levy, G.J., Downie, A., Crosky, A., Munroe, P., Lehmann, J., Joseph, S., Zhou, J., Wang, J.-J., Baudon, A., Chow, A.T., Calderón, F., Haddix, M., Conant, R., Magrini-Bair, K., Paul, E., Wouters, K., Woolf, D., Amonette, J.E., Street-Perrott, F.A., Lehmann, J., Joseph, S., Singh, B.P., Cowie, A.L., Zimmerman, A.R., Gao, B., Ahn, M.-Y., Spokas, K.A., Reicosky, D.C., Schmidt, M.W.I., Kögel-Knabner, I., Vogel, C., Le Guillou, C., Angers, D.A., Maron, P.A., Leterme, P., Menasseri-Aubry, S., Kleber, M., Sollins, P., Sutton, R., Méndez, A., Tarquis, A.M., Saa-Requejo, A., Guerrero, F., Gascó, G., Deenik, J.L., McClellan, T., Uehara, G., Antal, M.J., Campbell, S., Spokas, K.A., Smebye, A., Jamieson, T., Sager, E., Guéguen, C., Lin, Y., Munroe, P., Joseph, S., Kimber, S., Van Zwieten, L., Lehmann, J., Kleber, M., Kookana, R.S., Brunauer, S., Emmett, P.H., Teller, E., Bufflap, S.E., Allen, H.E., Miller, M.P., McKnight, D.M., Murphy, K.R., Stedmon, C.A., Graeber, D., Bro, R., Stedmon, C.A., Bro, R., Zsolnay, A., Baigar, E., Jimenez, M., Steinweg, B., Saccomandi, F., Petrone, K.C., Fellman, J.B., Hood, E., Donn, M.J., Grierson, P.F., Berggren, M., Laudon, H., Jansson, M., Miller, M.P., McKnight, D.M., Chapra, S.C., Williams, M.W., 2016. Biochar affects carbon composition and stability in soil: a combined spectroscopy-microscopy study. Sci. Rep. 6, 25127. https://doi.org/10.1038/srep25127.

Heymann, K., Lehmann Johannes, J., Solomon, D., Schmidt, M.W.I., Regier, T., 2011. C 1s K-edge near edge X-ray absorption fine structure (NEXAFS) spectroscopy for characterizing functional group chemistry of black carbon. Org. Geochem. 42, 1055–1064. https://doi.org/10.1016/j.orggeochem.2011.06.021.

IBI, 2015. Standardized product definition and product testing guidelines for biochar that is used in soil. Int. Biochar Initiat. 22 (doi:http://www.biochar-international.org/characterizationstandard).

Kaal, J., Rumpel, C., 2009. Can pyrolysis-GC/MS be used to estimate the degree of thermal alteration of black carbon? Org. Geochem. 40, 1179–1187. https://doi.org/10.1016/j.orggeochem.2009.09.002.

Kaal, J., Nierop, K.G.J., Kraal, P., Preston, C.M., 2012a. A first step towards identification of tannin-derived black carbon: conventional pyrolysis (Py-GC-MS) and thermally assisted hydrolysis and methylation (THM-GC-MS) of charred condensed tannins. Org. Geochem. 47, 99–108. https://doi.org/10.1016/j.orggeochem.2012.03.009.

Kaal, J., Schneider, M.P.W., Schmidt, M.W.I., 2012b. Rapid molecular screening of black carbon (biochar) thermosequences obtained from chestnut wood and rice straw: a pyrolysis-GC/MS study. Biomass Bioenergy 45, 115–129. https://doi.org/10.1016/j.biombioe.2012.05.021.

Keiluweit, M., Nico, P.S., Johnson, M.G., Kleber, M., 2010. Dynamic molecular structure of plant biomass-derived black carbon (biochar). Environ. Sci. Technol. 44, 1247–1253. https://doi.org/10.1021/es9031419.

Keiluweit, M., Kleber, M., Sparrow, M.A., Simoneit, B.R.T., Prahl, F.G., 2012. Solvent-extractable polycyclic aromatic hydrocarbons in biochar: influence of pyrolysis temperature and feedstock. Environ. Sci. Technol. 46, 9333–9341. https://doi.org/10.1021/es302125k.

Klasson, K.T., 2017. Biochar characterization and a method for estimating biochar quality from proximate analysis results. Biomass Bioenergy 96, 50–58. https://doi.org/10.1016/j.biombioe.2016.10.011.

Knicker, H., Müller, P., Hilscher, A., 2007. How useful is chemical oxidation with dichromate for the determination of "Black Carbon" in fire-affected soils? Geoderma 142, 178–196. https://doi.org/10.1016/j.geoderma.2007.08.010.

Kusumo, B., Arbestain, M., Mahmud, A., Hedley, M., Hedley, C., Pereira, R., Wang, T., Singh, B., 2014. Assessing biochar stability indices using near infrared spectroscopy. J. Near Infrared Spectrosc. 22, 313–328. https://doi.org/10.1255/jnirs.1125.

Kuzyakov, Y., Bogomolova, I., Glaser, B., 2014. Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific ^{14}C analysis. Soil Biol. Biochem. 70, 229–236. https://doi.org/10.1016/j.soilbio.2013.12.021.

Laird, D.A., Brown, R.C., Amonette, J.E., Lehmann, J., 2009. Review of the pyrolysis platform for coproducing bio-oil and biochar. Biofuels Bioprod. Biorefin. 3, 547–562. https://doi.org/10.1002/bbb.169.

Leal, O.A., 2015. Impacto Da Adição De Carbono Pirogênico Nas Propriedades Químicas Do Solo E Na Qualidade E Quantidade De Matéria Orgânica De Um Cambissolo Subtropical E De Um Argissolo Tropical. Universidade Federal do Río Grande do Sul.

Lehmann, J., 2007a. Bio-energy in the black. Front. Ecol. Environ. 5, 381–387. https://doi.org/10.1890/1540-9295(2007)5[381:BITB]2.0.CO;2.
Lehmann, J., 2007b. A handful of carbon. Nature 447, 143–144. https://doi.org/10.1038/447143a.
Lehmann, J., Joseph, S. (Eds.), 2015. Biochar for Environmental Management: Science, Technology and Implementation, 2nd ed. Routledge, London and New York https://doi.org/10.4324/9781849770552.
Lehmann, J., Kleber, M., 2015. The contentious nature of soil organic matter. Nature, 1–9 https://doi.org/10.1038/nature16069.
Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems - a review. Mitig. Adapt. Strateg. Glob. Chang. 11, 403–427. https://doi.org/10.1007/s11027-005-9006-5.
Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., Coleman, K., Woodbury, P., Krull, E., 2008. Australian climate-carbon cycle feedback reduced by soil black carbon. Nat. Geosci. 1, 832–835. https://doi.org/10.1038/Ngeo358.
Leifeld, J., 2007. Thermal stability of black carbon characterised by oxidative differential scanning calorimetry. Org. Geochem. 38, 112–127. https://doi.org/10.1016/j.orggeochem.2006.08.004.
Leng, L., Yuan, X., Huang, H., Wang, H., Wu, Z., Fu, L., Peng, X., 2015a. Characterization and application of bio-chars from liquefaction of microalgae, lignocellulosic biomass and sewage sludge. Fuel Process. Technol. 129, 8–14. https://doi.org/10.1016/j.fuproc.2014.08.016.
Leng, L., Yuan, X., Zeng, G., Shao, J., Chen, X., Wu, Z., Wang, H., Peng, X., 2015b. Surface characterization of rice husk bio-char produced by liquefaction and application for cationic dye (Malachite green) adsorption. Fuel 155, 77–85. https://doi.org/10.1016/j.fuel.2015.04.019.
Leng, L., Li, H., Yuan, X., Zhou, W., Huang, H., 2018a. Bio-oil upgrading by emulsification/microemulsification: a review. Energy 161, 214–232. https://doi.org/10.1016/j.energy.2018.07.117.
Leng, L., Li, J., Wen, Z., Zhou, W., 2018b. Use of microalgae to recycle nutrients in aqueous phase derived from hydrothermal liquefaction process. Bioresour. Technol. 256, 529–542. https://doi.org/10.1016/j.biortech.2018.01.121.
Leng, L., Li, J., Yuan, X., Li, J., Han, P., Hong, Y., Wei, F., Zhou, W., 2018c. Beneficial synergistic effect on bio-oil production from co-liquefaction of sewage sludge and lignocellulosic biomass. Bioresour. Technol. 251, 49–56. https://doi.org/10.1016/j.biortech.2017.12.018.
Li, H., Wang, S., Yuan, X., Xi, Y., Huang, Z., Tan, M., Li, C., 2018. The effects of temperature and color value on hydrochars' properties in hydrothermal carbonization. Bioresour. Technol. 249, 574–581. https://doi.org/10.1016/j.biortech.2017.10.046.
Li, Y., Yuan, X., Wang, D., Wang, H., Wu, Z., Jiang, L., Mo, D., Yang, G., Guan, R., Zeng, G., 2018. Recyclable zero-valent iron activating peroxymonosulfate synchronously combined with thermal treatment enhances sludge dewaterability by altering physico-chemical and biological properties. Bioresour. Technol. 262, 294–301. https://doi.org/10.1016/j.biortech.2018.04.050.
Liang, B., Lehmann, J., Solomon, D., Sohi, S., Thies, J.E., Skjemstad, J.O., Luizão, F.J., Engelhard, M.H., Neves, E.G., Wirick, S., 2008. Stability of biomass-derived black carbon in soils. Geochim. Cosmochim. Acta 72, 6069–6078. https://doi.org/10.1016/j.gca.2008.09.028.
Lu, L., Sahajwalla, V., Harris, D., 2000. Characteristics of chars prepared from various pulverized coals at different temperatures using drop-tube furnace. Energy Fuel 14, 869–876. https://doi.org/10.1021/ef990236s.
Manyà, J.J., Laguarta, S., Ortigosa, M.A., Manso, J.A., 2014a. Biochar from slow pyrolysis of two-phase olive mill waste: effect of pressure and peak temperature on its potential stability. Energy Fuel 28, 3271–3280. https://doi.org/10.1021/ef500654t.
Manyà, J.J., Ortigosa, M.A., Laguarta, S., Manso, J.A., 2014b. Experimental study on the effect of pyrolysis pressure, peak temperature, and particle size on the potential stability of vine shoots-derived biochar. Fuel 133, 163–172. https://doi.org/10.1016/j.fuel.2014.05.019.
Mašek, O., Brownsort, P., Cross, A., Sohi, S., 2013. Influence of production conditions on the yield and environmental stability of biochar. Fuel 103, 151–155. https://doi.org/10.1016/j.fuel.2011.08.044.
McBeath, A.V., Smernik, R.J., Schneider, M.P.W., Schmidt, M.W.I., Plant, E.L., 2011. Determination of the aromaticity and the degree of aromatic condensation of a thermosequence of wood charcoal using NMR. Org. Geochem. 42, 1194–1202. https://doi.org/10.1016/j.orggeochem.2011.08.008.
McBeath, A.V., Wurster, C.M., Bird, M.I., 2015. Influence of feedstock properties and pyrolysis conditions on biochar carbon stability as determined by hydrogen pyrolysis. Biomass Bioenergy 73, 155–173. https://doi.org/10.1016/j.biombioe.2014.12.022.
McKendry, P., 2002. Energy production from biomass (part 1): overview of biomass. Bioresour. Technol. 83, 37–46.
Naisse, C., Alexis, M., Plante, A., Wiedner, K., Glaser, B., Pozzi, A., Carcaillet, C., Criscuoli, I., Rumpel, C., 2013. Can biochar and hydrochar stability be assessed with chemical methods? Org. Geochem. 60, 40–44. https://doi.org/10.1016/j.orggeochem.2013.04.011.
Nguyen, B.T., Lehmann, J., Hockaday, W.C., Joseph, S., Masiello, C.A., 2010. Temperature sensitivity of black carbon decomposition and oxidation. Environ. Sci. Technol. 44, 3324–3331. https://doi.org/10.1021/es903016y.
Rombolà, A.G., Fabbri, D., Meredith, W., Snape, C.E., Dieguez-Alonso, A., 2016. Molecular characterization of the thermally labile fraction of biochar by hydropyrolysis and pyrolysis-GC/MS. J. Anal. Appl. Pyrolysis 121, 230–239. https://doi.org/10.1016/j.jaap.2016.08.003.
Rumpel, C., González-Pérez, J.A., Bardoux, G., Largeau, C., Gonzalez-Vila, F.J., Valentin, C., 2007. Composition and reactivity of morphologically distinct charred materials left after slash-and-burn practices in agricultural tropical soils. Org. Geochem. 38, 911–920. https://doi.org/10.1016/j.orggeochem.2006.12.014.
Singh, B.P., Cowie, A.L., Smernik, R.J., 2012. Biochar carbon stability in a clayey soil as a function of feedstock and pyrolysis temperature. Environ. Sci. Technol. 46, 11770–11778. https://doi.org/10.1021/es302545b.
Singh, N., Abiven, S., Torn, M.S., Schmidt, M.W.I., 2012. Fire-derived organic carbon in soil turns over on a centennial scale. Biogeosciences 9, 2847–2857. https://doi.org/10.5194/bg-9-2847-2012.
Singh, B., Fang, Y., Cowie, B.C.C., Thomsen, L., 2014. NEXAFS and XPS characterisation of carbon functional groups of fresh and aged biochars. Org. Geochem. 77, 1–10. https://doi.org/10.1016/j.orggeochem.2014.09.006.
Spokas, K.A., 2010. Review of the stability of biochar in soils: predictability of O:C molar ratios. Carbon Manag. 1, 289–303. https://doi.org/10.4155/cmt.10.32.
Suárez-Abelenda, M., Kaal, J., McBeath, A.V., 2017. Translating analytical pyrolysis fingerprints to Thermal Stability Indices (TSI) to improve biochar characterization by pyrolysis-GC-MS. Biomass Bioenergy 98, 306–320. https://doi.org/10.1016/j.biombioe.2017.01.021.
Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., Yang, Z., 2015. Application of biochar for the removal of pollutants from aqueous solutions. Chemosphere 125, 70–85. https://doi.org/10.1016/j.chemosphere.2014.12.058.
Wang, T., Camps-Arbestain, M., Hedley, M., 2013. Predicting C aromaticity of biochars based on their elemental composition. Org. Geochem. 62, 1–6. https://doi.org/10.1016/j.orggeochem.2013.06.012.
Wang, J., Xiong, Z., Kuzyakov, Y., 2016. Biochar stability in soil: meta-analysis of decomposition and priming effects. GCB Bioenergy 8, 512–523. https://doi.org/10.1111/gcbb.12266.
Wang, S., Dai, G., Yang, H., Luo, Z., 2017. Lignocellulosic biomass pyrolysis mechanism: a state-of-the-art review. Prog. Energy Combust. Sci. 62, 33–86. https://doi.org/10.1016/j.pecs.2017.05.004.
Wang, T., Zhai, Y., Zhu, Y., Peng, C., Xu, B., Wang, T., Li, C., Zeng, G., 2018. Influence of temperature on nitrogen fate during hydrothermal carbonization of food waste. Bioresour. Technol. 247, 182–189. https://doi.org/10.1016/j.biortech.2017.09.076.
Wang, Y., Jiang, L., Dai, L., Yu, Z., Liu, Y., Ruan, R., Fu, G., Zhou, Y., Fan, L., Duan, D., Zhao, Y., 2018. Microwave-assisted catalytic co-pyrolysis of soybean straw and soapstock for bio-oil production using SiC ceramic foam catalyst. J. Anal. Appl. Pyrolysis 133, 76–81. https://doi.org/10.1016/j.jaap.2018.04.018.
Weng, Z. (Han), Van Zwieten, L., Singh, B.P., Tavakkoli, E., Joseph, S., Macdonald, L.M., Rose, T.J., Rose, M.T., Kimber, S.W.L., Morris, S., Cozzolino, D., Araujo, J.R., Archanjo, B.S., Cowie, A., 2017. Biochar built soil carbon over a decade by stabilizing rhizodeposits. Nat. Clim. Chang. 7, 371–376. https://doi.org/10.1038/nclimate3276.
Wiedemeier, D.B., Abiven, S., Hockaday, W.C., Keiluweit, M., Kleber, M., Masiello, C.A., McBeath, A.V., Nico, P.S., Pyle, L.A., Schneider, M.P.W., Smernik, R.J., Wiesenberg, G.L.B., Schmidt, M.W.I., 2015a. Aromaticity and degree of aromatic condensation of char. Org. Geochem. 78, 135–143. https://doi.org/10.1016/j.orggeochem.2014.10.002.
Wiedemeier, D.B., Brodowski, S., Wiesenberg, G.L.B., 2015b. Pyrogenic molecular markers: linking PAH with BPCA analysis. Chemosphere 119, 432–437. https://doi.org/10.1016/j.chemosphere.2014.06.046.
Wiesenberg, G.L.B., Lehndorff, E., Schwark, L., 2009. Thermal degradation od rye and maize straw: lipid pattern changes as a function of temperature. Org. Geochem. 40, 167–174.
Windeatt, J.H., Ross, A.B., Williams, P.T., Forster, P.M., Nahil, M.A., Singh, S., 2014. Characteristics of biochars from crop residues: potential for carbon sequestration and soil amendment. J. Environ. Manag. 146, 189–197. https://doi.org/10.1016/j.jenvman.2014.08.003.
Woolf, D., Lehmann, J., Joseph, S., Campbell, C., Christo, F.C., Angenent, L.T., 2017. An open-source biomass pyrolysis reactor. Biofuels Bioprod. Biorefin. 6, 246–256. https://doi.org/10.1002/bbb.1814.
Wurster, C.M., Saiz, G., Schneider, M.P.W., Schmidt, M.W.I., Bird, M.I., 2013. Quantifying pyrogenic carbon from thermosequences of wood and grass using hydrogen pyrolysis. Org. Geochem. 62, 28–32. https://doi.org/10.1016/j.orggeochem.2013.06.009.
Xu, X., Hu, X., Ding, Z., Chen, Y., 2017. Effects of copyrolysis of sludge with calcium carbonate and calcium hydrogen phosphate on chemical stability of carbon and release of toxic elements in the resultant biochars. Chemosphere 189, 76–85. https://doi.org/10.1016/j.chemosphere.2017.09.021.
Yang, H., Sheng, K., 2012. Characterization of biochar properties affected by different pyrolysis temperatures using visible-near-infrared spectroscopy. ISRN Spectrosc. 2012, 1–7. https://doi.org/10.5402/2012/712837.
Yang, F., Zhao, L., Gao, B., Xu, X., Cao, X., 2016. The interfacial behavior between biochar and soil minerals and its effect on biochar stability. Environ. Sci. Technol. 50, 2264–2271. https://doi.org/10.1021/acs.est.5b03656.
Zhang, C., Lai, C., Zeng, G., Huang, D., Yang, C., Wang, Y., Zhou, Y., Cheng, M., 2016. Efficacy of carbonaceous nanocomposites for sorbing ionizable antibiotic sulfamethazine from aqueous solution. Water Res. 95, 103–112. https://doi.org/10.1016/j.watres.2016.03.014.
Zhao, L., Cao, X., Mašek, O., Zimmerman, A., 2013. Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. J. Hazard. Mater. 256–257, 1–9. https://doi.org/10.1016/j.jhazmat.2013.04.015.
Zimmerman, A.R., 2010. Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). Environ. Sci. Technol. 44, 1295–1301. https://doi.org/10.1021/es903140c.
Zimmerman, A.R., Gao, B., Ahn, M.Y., 2011. Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. Soil Biol. Biochem. 43, 1169–1179. https://doi.org/10.1016/j.soilbio.2011.02.005.
Zimmermann, M., Bird, M.I., Wurster, C., Saiz, G., Goodrick, I., Barta, J., Capek, P., Santruckova, H., Smernik, R., 2012. Rapid degradation of pyrogenic carbon. Glob. Chang. Biol. 18, 3306–3316. https://doi.org/10.1111/j.1365-2486.2012.02796.x.
Zornoza, R., Moreno-Barriga, F., Acosta, J.A., Muñoz, M.A., Faz, A., 2016. Stability, nutrient availability and hydrophobicity of biochars derived from manure, crop residues, and municipal solid waste for their use as soil amendments. Chemosphere 144, 122–130. https://doi.org/10.1016/j.chemosphere.2015.08.046.